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(54) **Orthodontic bracket consisting of monocrystalline alpha-alumina.**

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(73) Proprietor : **Johnson & Johnson Dental Products Company**
Lake Shore Drive
East Windsor New Jersey (US)

(72) Inventor : **De Luca, Robert David**
108 Howard Way
Pennington New Jersey 08534 (US)
Inventor : **Jones, Robin Mackay Forbes**
302 Pennington-Titusville Road
Titusville New Jersey 08560 (US)

(74) Representative : **Jones, Alan John et al**
CARPMAELS & RANSFORD 43 Bloomsbury Square
London, WC1A 2RA (GB)

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Description

The invention relates to an orthodontic bracket of essentially monocrystalline alpha alumina, a surface of which is adapted to be bonded to a substrate by an adhesive.

5 In our European patent application No. 0 161 831 (Filing No. 85302978.5) there are disclosed orthodontic brackets comprising as a load bearing member essentially monocrystalline alpha alumina. As is disclosed in said application, one of the problems inherent in the use of essentially monocrystalline alpha alumina orthodontic brackets is bonding them to teeth (or to any other substrate) because of the high surface energy of essentially monocrystalline alpha alumina.

10 This invention relates to one means for enhancing the bond of essentially monocrystalline alpha alumina to substrates.

The semi-conductor art has disclosed articles made of single crystal alumina having a coating of silica. For instance, see US-A-3 764 507.

15 US-A-3 625 740, discloses a process for treating a sapphire surface with a silane to enhance adhesion to an epoxy resin.

The invention provides an orthodontic bracket of essentially monocrystalline alpha alumina a surface of which is adapted to be bonded to a substrate by an adhesive, characterised in that at least a portion of the surface to be bonded to the substrate is coated with a thin adherent coating of siliceous material comprising silica or glass containing at least 50 mole % of SiO₂ for which the adhesive has an affinity.

20 In the accompanying drawings:

Figure 1 is a perspective view of an orthodontic bracket made of essentially monocrystalline alpha alumina;

Figure 2 is a side view of the bracket of Figure 1;

Figure 3 is a front view of the bracket of Figure 1;

Figure 4 is a top view of bracket of Figure 1;

25 Figure 5 is a top view of a die that is used to produce an essentially monocrystalline alpha alumina rod having cross-sectional configuration essentially identical to the configuration of the top of said die;

Figure 6 is a schematic representation of apparatus for producing an essentially monocrystalline alpha alumina rod;

30 Figure 7 is a perspective view of an essentially monocrystalline alpha alumina rod produced by the apparatus of Figure 6;

Figure 8 is a perspective view of a bracket blank cut from the essentially monocrystalline alpha alumina rod of Figure 7;

Figure 9 is a schematic representation of apparatus for sputter coating silica on an essentially monocrystalline alpha alumina article;

35 Figure 10 is a perspective view of a plastic orthodontic bracket having an essentially monocrystalline alpha alumina liner in the archwire groove;

Figure 11 is a perspective view of an orthodontic bracket having a plastic base, with the remainder of the bracket being essentially monocrystalline alpha alumina;

Figure 12 is a view similar to Figure 5, showing an alternative configuration of the top of the die;

40 Figure 13 is a perspective view of an essentially monocrystalline alpha alumina orthodontic bracket having a keyway in the base for the purpose of enhancing the bonding of the bracket to the tooth;

Figure 14 is a side view of the orthodontic bracket of Fig. 13; and

Figure 15 is a perspective view of a "single-wing" orthodontic bracket made of essentially monocrystalline alpha alumina.

45 As used herein, the term "essentially monocrystalline alpha alumina" describes alpha alumina comprised of a single crystal or two or more single crystals grown together longitudinally but separated by a relatively small angle (usually within 4°, determined with respect to the C-axes of the neighboring single crystals) grain boundary.

50 Preferably, the orthodontic bracket is entirely essentially monocrystalline alpha alumina. Such a bracket can be produced by first drawing an essentially monocrystalline alpha alumina rod from a melt, wherein the rod has a predetermined cross-sectional configuration, by slicing the rod into individual blanks, and then machining the blanks to produce the bracket. A detailed description of this process follows.

55 The preferred procedure for producing an essentially monocrystalline alpha alumina rod having predetermined cross-sectional configuration is the EFG (for Edge-defined, Film-fed, Growth) modification of the Czochralski process for growing essentially monocrystalline alpha alumina. The EFG process is described by LaBelle in "EFG - The invention and Application to Sapphire Growth", in Journal of Crystal Growth, 50, pages 8-17 (September 1980). See also US-A-3 591 348, US-A-3 701 636, US-A-3 915 662 and other patents and articles cited in the Journal of Crystal Growth article.

Figure 6 is a schematic representation of apparatus for producing an essentially monocrystalline alpha alumina rod having a predetermined cross-sectional configuration by the EFG process. The apparatus 20 includes a crucible 22 containing molten alumina 24. A die 26 made from a suitable material such as molybdenum or iridium is positioned such that the bottom of the die 26 is immersed in the molten alumina 24, and the top of the die 26 is above the surface of the melt 24. A vertical distance above the melt 24 of up to 50 millimeters is permissible. Figure 5 shows the top surface 28 of the die 26. The top surface 28 is smooth, flat, and has the shape of the desired configuration of the cross-section of the essentially monocrystalline alpha alumina rod 30 (shown in Figure 7) from which the brackets are made. It is important that the side 32 of the die 26 and the top surface of the die meet in a sharp 90° angle, in order to minimize imperfections in the surface of the growing rod 30. The die 26 contains a capillary passage 34 through which molten alumina 24 is drawn. The melt 24 is drawn from the crucible 22 through the capillary 34 to the top surface 28 of the die 26, where it spreads out and completely covers the said top surface 28 with a film of molten alumina. However, because molten alumina and molybdenum or iridium have the appropriate wettability relationship, the molten alumina film stops at the edge of the surface 28. Therefore, alpha-alumina crystal grown or pulled from this film of molten alumina assumes a cross-sectional configuration substantially exactly the same as the configuration of the top surface 28 of the die 26. Thus, the rod 30 (which had been started by a seed crystal, as in the Czochralski process) pulled by a pulling mechanism 36 from the film of molten alumina on the top surface 28 of the die 26 will have a cross-sectional configuration substantially identical to the configuration of the top surface 28 of the die 26.

The crystal orientation of the growing rod may prove to be important (at least economically, and perhaps also from a performance standpoint) in the practice of the invention. In the case of essentially monocrystalline alpha alumina the crystal orientation can be defined with reference to the C axis of the crystal. (The C axis is perpendicular to the plane which contains the simplest arrangement of atoms in the crystal unit cell. Stated another way, the C axis is perpendicular to the plane which contains the a_1 and a_2 axes). The minimum amount of strain developed in the growing crystal will occur if the C axis is found in a plane perpendicular to the longitudinal axis L of the rod 30 (see Figure 7). This may prove to be the optimum crystal orientation in some cases. (As is known in the art, the growing crystal will assume the crystal orientation of the seed crystal).

In other cases, however, it may be preferred to orient the C axis an angle α from the longitudinal axis L of the rod 30 (Figure 7) such that the C axis is found in a conical surface formed by pivoting the C axis 360° around any point of intersection between the C axis and the longitudinal axis L, with the angle between L and the C axis being α . In this case, the angle α is between 30° and 60°. The reason for orienting the crystal in this way is to minimize chipping of the essentially monocrystalline alpha alumina during machining.

Regardless of the crystal orientation of the rod 30, it is preferred to anneal the rod 30 prior to machining so as to relieve stresses in the crystal to minimize the chances of breakage during machining. A typical annealing cycle would be to heat the rod 30 from room temperature up to 1850°C at an even rate for about 12 hours, to maintain the rod 30 at 1850°C for 4 to 6 hours, and to then cool the rod 30 down to room temperature at an even rate for 18 to 24 hours.

The essentially monocrystalline alpha alumina rod 30 is cut into individual blanks 38 (Figure 8), each of which is machined into a bracket. Figures 1-4 are various views of an orthodontic bracket 40 made completely of essentially monocrystalline alpha alumina. The bracket 40 is made from the blank 38 by a series of cutting, grinding, and polishing steps, using known techniques for machining essentially monocrystalline alpha alumina. A diamond cutting wheel or an abrasive slurry wire saw may be used to cut out the archwire groove 42 and the "saddle" 43 of a double wing bracket (such as is shown in Figure 1). A single wing bracket 41 is shown in Figure 15. Edges may be beveled by grinding, and corners rounded off by polishing, by known techniques. After machining, another annealing step under the conditions suggested above is recommended to relieve stresses induced by machining.

As is shown in the drawings, the tooth contacting surface 74 of the bracket is contoured to match the curved surface of a tooth. This contour is machined by a conventional grinding procedure.

In alternative embodiments, the most critical load bearing portions of the bracket are made of essentially monocrystalline alpha alumina, while the remainder is made of another transparent material, such as polycarbonate or polysulfone plastic, that is less expensive, easier to work, and easier to bond to the tooth. Figure 10 shows one such alternative embodiment, wherein the bracket 44 is made predominantly of transparent plastic 46 (e.g., polycarbonate), but wherein the archwire groove has a crystalline alpha-alumina liner 48 cemented therein by an adhesive in accordance with this invention. In another embodiment, shown in Figure 11, the bracket 50 has a transparent plastic base 52 cemented to an essentially monocrystalline alpha alumina body 54 by an adhesive in accordance with this invention. In both of these alternative embodiments, the essentially monocrystalline alpha alumina portions can be made by a modification of the method described above, starting with an essentially monocrystalline alpha alumina rod of appropriate shape made by the EFG process.

As was indicated above, bonding an essentially monocrystalline alpha alumina bracket to the tooth (or to

a plastic base or to any other substrate) is not a straightforward matter. essentially monocrystalline alpha alumina has a high surface energy, and many of the ordinary orthodontic cements (which are usually acrylic resins) will not adhere well enough to essentially monocrystalline alpha alumina to be useable without taking steps to enhance the adhesion. One means of enhancing the adhesion of an essentially monocrystalline alpha alumina bracket to the tooth is illustrated in Figs. 13 and 14, in which a bracket 56 is shown that has an undercut or keyway 58 in the bottom or tooth-contacting surface 74 of the bracket 56. Orthodontic cement filling the keyway 58 will have enhanced mechanical adhesion to the bracket 56 because of the undercut portion. This bracket 56 can be made by a method analogous to that described above, starting with the EFG process using a molybdenum die 60 having a top surface shaped as shown in Figure 12.

This invention provides another means of enhancing the adhesion of cements such as acrylic resins to a crystalline alumina bracket by altering the surface of the essentially monocrystalline alpha alumina in such a way as to increase the strength of the adhesive bond between the essentially monocrystalline alpha alumina and the cement. It is known, for instance, that a wide variety of silicone coupling agents can be used to enhance the adhesive force between siliceous substrates and a wide variety of thermosetting plastics. However, such known technology may not be adequate in the present case, because the known coupling agents may not enhance the bond of acrylic cements to essentially monocrystalline alpha alumina to the strength required in an orthodontic application. The lack of availability of adequate coupling agents for essentially monocrystalline alpha alumina is circumvented in accordance with this invention by coating the essentially monocrystalline alpha alumina surface that is to be in contact with the cement with a thin coating (usually thinner than about 1 μ m (10,000 angstroms), and preferably, up to about 100 nm (1,000 angstroms)) of a siliceous material such as silica, and then using silicone coupling agents to enhance the bond of that surface to the cement, in a manner analogous to that which is presently known. Examples of means for coating the essentially monocrystalline alpha alumina surface with a siliceous material are cathode sputtering, plasma deposition, and electron beam evaporation, all of which are known techniques, especially in the semi-conductor arts. Figure 9 is a schematic representation of apparatus suitable for sputter coating silica onto the surface of an essentially monocrystalline alpha alumina orthodontic bracket. The apparatus, shown generally as 62, includes a sputtering chamber 64 (which is vacuum tight), a target 66, in this case silicon metal, which is brought to cathode potential, an RF or DC power supply 68, and a plate 70 for holding the cleaned and dried substrate 72 to be coated, in which the plate 70 is brought to anode potential. A source of oxygen (not shown) introduces oxygen into the chamber 64 so that the silicon metal 66 will be converted to silicon dioxide 80 on the substrate 72. Reactive sputtering, such as is briefly outlined here, is known. For instance, see "The Basics of Sputtering", printed in December 1980 by Materials Research Corporation, Orangeburg, New York 10962.

The essentially monocrystalline alpha alumina bracket having its base surface 74 (see Figure 2) sputter coated with silica or other siliceous material such as a glass, has a greatly enhanced affinity for silane or silicone coupling agents such as gamma-methacryloxypropyltrimethoxysilane, and by using such coupling agents the adhesion of the bracket to acrylic orthodontic cements is greatly enhanced. This is illustrated in the Examples, below:

Example 1 and Control Examples 1-6

The purpose of the experiments described below was to measure the shear strength between various materials and a plug of adhesive. The experiments were carried out by inserting an essentially monocrystalline alpha alumina 0.51 cm (0.2 inch) diameter rod for a steel rod, to simulate a steel orthodontic bracket) treated in various ways into the end of a short length of "Tygon" laboratory tubing, and then building up a plug of an acrylic orthodontic cement on the end of the rod by tamping it into the tubing against the end of the rod. After the cement hardened, the shear strength between the rod and the cement was measured by the test procedure described below.

The acrylic orthodontic cement used was a two-paste formulation having the following composition:

	Component	Weight Per Cent	
		Universal Catalyst	
5	2,2-bis[4-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane ("Bis-GMA")	12.60	12.80
	Bisphenol-A Dimethacrylate	1.40	1.42
10	Triethyleneglycol Dimethacrylate	6.09	6.09
	2-Hydroxy-4-methoxybenzophenone	0.20	0.20
	Butylated hydroxytoluene	0.01	0.03
15	N,N-di(2-hydroxyethyl)-p-toluidine	0.50	—
	Benzoyl Peroxide	—	0.40
	Quartz powder-silane treated	75.00	75.86
20	Fumed Colloidal Silica	3.20	3.20
	Pigments	1.00	—

25 Approximately equal quantities of the two pastes are mixed just before use, and a total of about 0.5 gram of the mixed cement is spatulated into the open end of the tubing and tamped against the end of the rod, to build up a short plug of cement. After the cement has hardened (within 3 to 5 minutes), the tubing is cut away and the sample is placed in water at 37°C for 48 hours, after which it is tested.

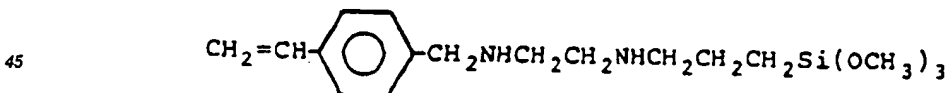
30 An Instron Testing Machine is used. The sample is placed on its side in a "V" shaped steel block and is clamped tightly therein. In this test, the cured cement is sheared off at the rod/cement interface with a steel blade secured to the cross head of the Instron machine. The blade was positioned as closely as possible to the interface, about 1/2 to 1 millimeter from the interface on the cement side thereof, and the shearing force exerted at the interface was determined using a cross head speed of 0.13 cm/minute (0.05 inch/minute).

The various samples tested were the following:

35 Control 1 - Mesh bonded stainless steel rod. The rod was stainless steel having a 0.177 mm aperture (80-mesh), square weave metal wire vacuum brazed on to the end of the rod.

Control 2 - Essentially monocrystalline alpha alumina rod, etched in sulfuric acid (20% aqueous) by boiling for 2 minutes (all of the Essentially monocrystalline alpha alumina rods were etched in sulfuric acid to thoroughly clean them prior to treatment, unless otherwise specified). This rod has no further treatment.

40 Control 3 - Essentially monocrystalline alpha alumina rod, treated with a 1% solution in ethanol of Z-6032 silane from Dow Corning. This silane has the following structure:



Control 4 - Essentially monocrystalline alpha alumina rod, treated with a 1% ethanol solution of gamma-methacryloxypropyltrimethoxysilane (A-174).

50 Control 5 - Essentially monocrystalline alpha alumina rod, treated with a 1% ethanol solution (based on weight of silane) of an epoxy/silane primer prepared as follows:

6.13 grams of A-1100 silane (gamma-aminopropyltriethoxysilane) and 19.3 grams of the diglycidyl diether of bisphenol-A were added to a reaction vessel and heated to 60°C. 4.77 grams of methacrylic acid was dripped into the mixture over a period of three hours. When the mixture became quite viscous, ethanol was added. At the conclusion of the methacrylic acid addition, more ethanol was added to reach a 1% solution, based on the silane.

55 Control 6 - Essentially monocrystalline alpha alumina rod treated with a Bis-GMA/silane primer that was prepared in the following manner:

91.9 millequivalents of Bis-GMA was reacted with 22.85 millimoles of A-1100 silane in the presence

of 5 drops of acetic acid, in ethanol solution in a Michael addition. The reaction product was applied to the sapphire in a 1% ethanol solution.

5 Example 1

Essentially monocrystalline alpha alumina rod coated with a layer of silica about 1 μm (10,000 Angstroms) thick by electron beam evaporation. (This rod was not acid-etched, since the electron beam treatment cleans the surface adequately). Prior to treating the silica-coated rod with a silane coupling agent, the coated rod is heated in air at 350°C for one hour. This converts the silica surface to a form that has a greater affinity for the silane. (It appears that silanol groups are thereby formed, the moisture content of air being sufficient to promote their formation). Heating in ethylene chloride also has the same effect, for reasons that are not clear. The silica coated rod was treated with a 1/2% ethanol solution of A-174 silane by spraying, followed by air drying. The silane is then hydrolyzed by immersion in water for one hour at room temperature.

15 The results of the shear tests are displayed below in Table I:

TABLE I

20	Sample	Shear Strength,	kg/cm ²
		Psi	
	Control 1	1630 (650)	114 (45.7)
	Control 2	570 (310)	40.1 (21.8)
25	Control 3	1010 (420)	71.0 (29.5)
	Control 4	700 (515)	49.2 (36.2)
	Control 5	1170 (320)	82.3 (22.5)
30	Control 6	970 (33)	68.2 (2.32)
	Example 1	1420 (165)	99.8 (11.6)

35 The values in parentheses were the standard deviations. Three specimens of each sample were tested. The value obtained for Control 1, the mesh bonded steel rod, is considered to be approximate maximum obtainable with the cement tested. In Control 1, the cement itself failed, rather than the interface.

As the foregoing experiment indicates, the addition of a thin, adherent coating of a siliceous material (in this case, silica) to the surface of essentially monocrystalline alpha alumina enables one to obtain a strong adhesive bond between essentially monocrystalline alpha alumina and adhesives. In the preferred way of practicing the invention, a silane coupling agent is used to enhance the bond between the siliceous coating and the adhesive. The type of silane that is used is dependent upon the nature of the adhesive, as is known in the art.

45 For instance, when an acrylic resin is used as the adhesive (or, indeed, any adhesive that cures by polymerization of an ethylenic double bond), the silane (e.g., A-174) will ordinarily contain an ethylenic double bond that interacts with the resin. If an epoxy adhesive is used, the silane (e.g., A-1100) will usually contain an amino group, preferably a primary amino group, which group will interact with the polymerizing epoxy resin. The principles of selecting a coupling agent to enhance the bond between a siliceous material and an adhesive are known, and the known principles are applicable here.

50 The siliceous coating on the essentially monocrystalline alpha alumina is preferably silica, but can also be other siliceous materials such as glasses, that contain significant amounts, usually at least 50 mole per cent, of silica. Other materials that can be present in the siliceous material include alkali metal oxides, alkaline earth metal oxides, boron oxide, lead oxide, alumina, rare earth metal oxides (to impart fluorescence), and the like.

55

Claims

1. An orthodontic bracket of essentially monocrystalline alpha alumina a surface of which is adapted to be

bonded to a substrate by an adhesive, characterised in that at least a portion of the surface to be bonded to the substrate is coated with a thin adherent coating of siliceous material comprising silica or glass containing at least 50 mole % of SiO_2 for which the adhesive has an affinity.

2. The bracket of claim 1 wherein the adhesive bond between said coating of siliceous material and the adhesive is enhanced by a silane coupling agent.
3. The bracket of claim 2 wherein the adhesive is an acrylic material and wherein the silane coupling agent contains ethylenic unsaturation.
4. The bracket of claim 2 wherein the adhesive is an epoxy resin and the silane coupling agent contains an amino group.

Patentansprüche

1. Orthodontische Klammer aus im wesentlichen monokristallinem alpha-Aluminiumoxid, deren eine Oberfläche zum Verbinden mit einem Substrat mittels eines Klebstoffes vorbereitet ist, dadurch gekennzeichnet, daß wenigstens ein Teil der mit dem Substrat zu verbindenden Oberfläche mit einem dünnen anhaftenden Überzug aus einem Siliziumdioxid oder Glas mit einem Gehalt an wenigstens 50 Mol-% SiO_2 umfassenden Kieselsäurematerial bedeckt ist, zu welchem Überzug der Klebstoff eine Affinität aufweist.
2. Klammer nach Anspruch 1, worin die Klebeverbindung zwischen dem Überzug aus Kieselsäurematerial und dem Klebstoff durch ein Silankupplungsmittel verbessert ist.
3. Klammer nach Anspruch 2, worin der Klebstoff ein Acrylmaterial ist und worin das Silankupplungsmittel eine ethylenische Unsättigung enthält.
4. Klammer nach Anspruch 2, worin der Klebstoff ein Epoxyharz ist und das Silankupplungsmittel eine Aminogruppe enthält.

Revendications

1. Arcade orthodontique en alumine essentiellement alpha monocristalline dont une surface doit pouvoir être liée à un substrat à l'aide d'un adhésif, caractérisé en ce qu'au moins une portion de la surface à lier au substrat est enduite d'une mince couche adhérente d'une matière siliceuse comprenant de la silice ou un verre contenant au moins 50 moles % de SiO_2 avec lequel l'adhésif a de l'affinité.
2. Arcade orthodontique selon la revendication 1, dans lequel la liaison adhésive entre ledit enduit en matière siliceuse et l'adhésif est améliorée par un agent silanique de couplage.
3. Arcade orthodontique selon la revendication 2, dans lequel l'adhésif est une matière acrylique et dans lequel l'agent silanique de couplage contient une insaturation éthylénique.
4. Arcade orthodontique selon la revendication 2, dans lequel l'adhésif est une résine époxy et l'agent silanique de couplage contient un groupe amino.

FIG-1

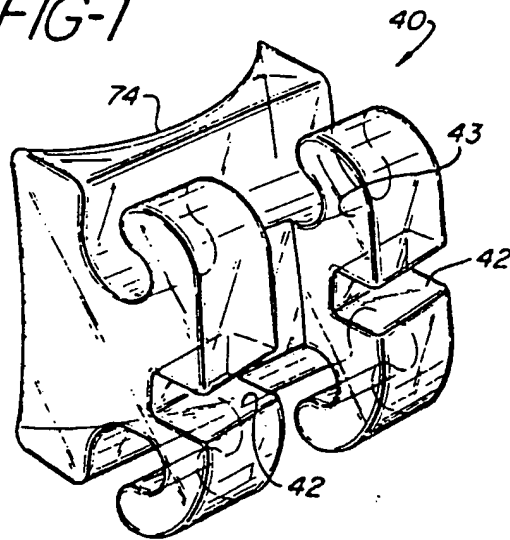


FIG-2

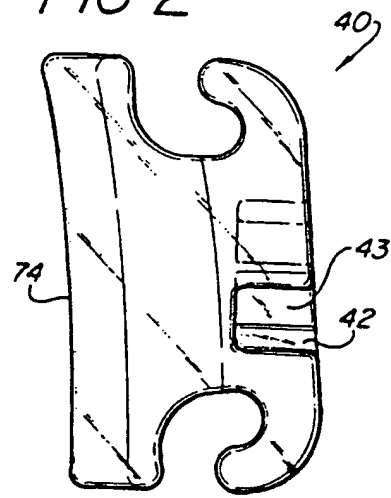


FIG-3

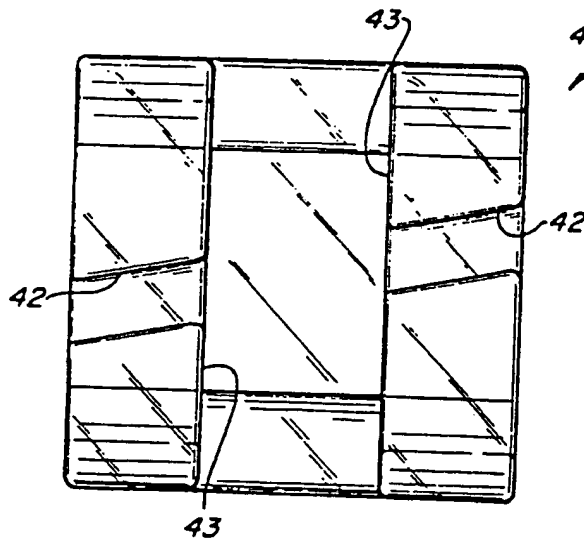


FIG-4

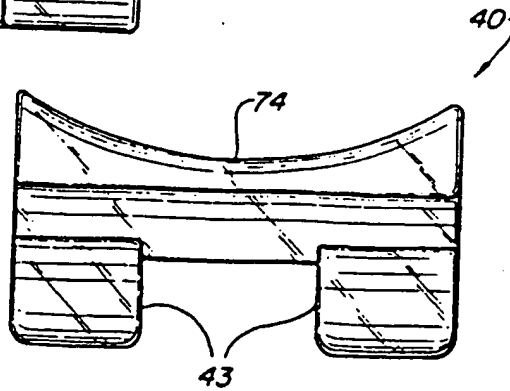


FIG-5

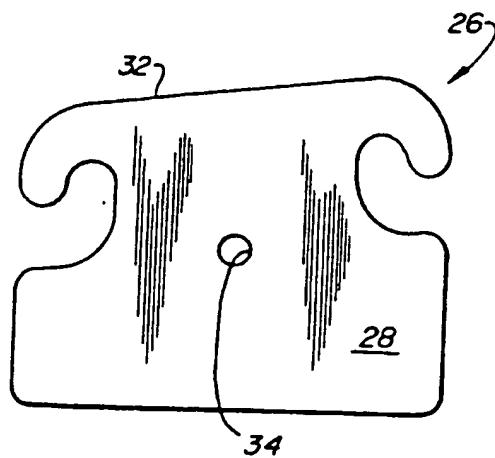
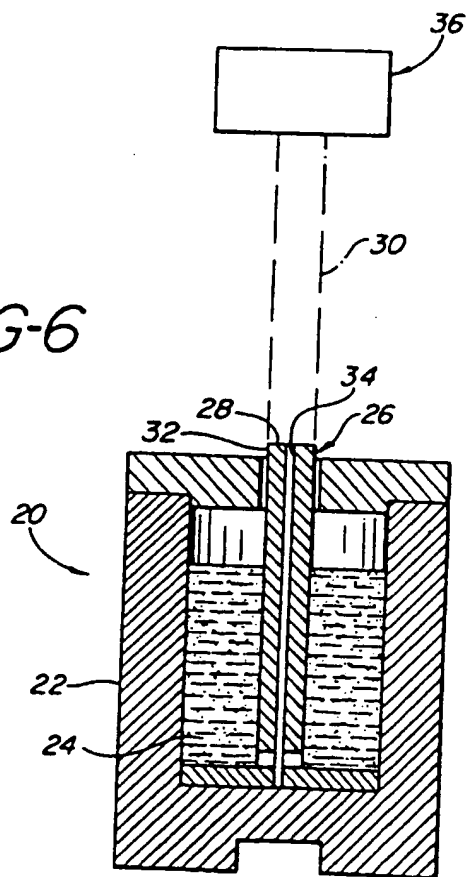


FIG-6



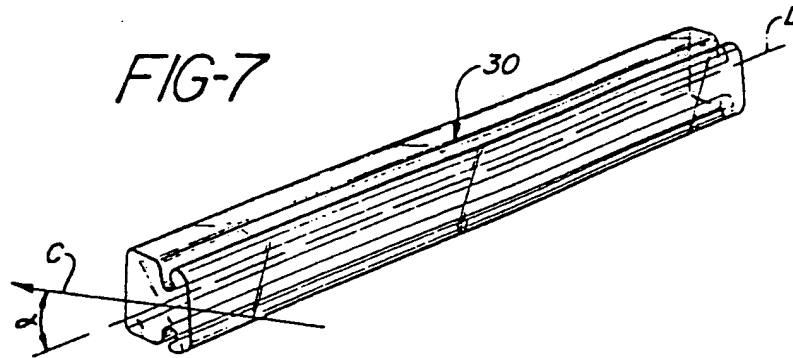


FIG-8

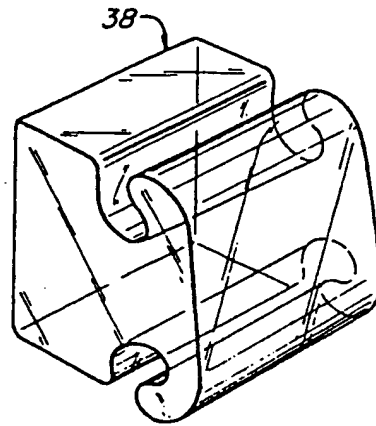


FIG-10

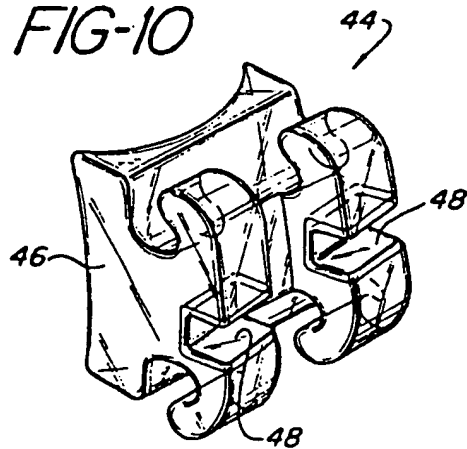


FIG-11

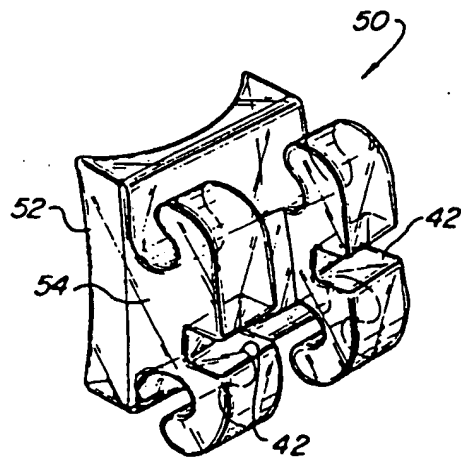


FIG-9

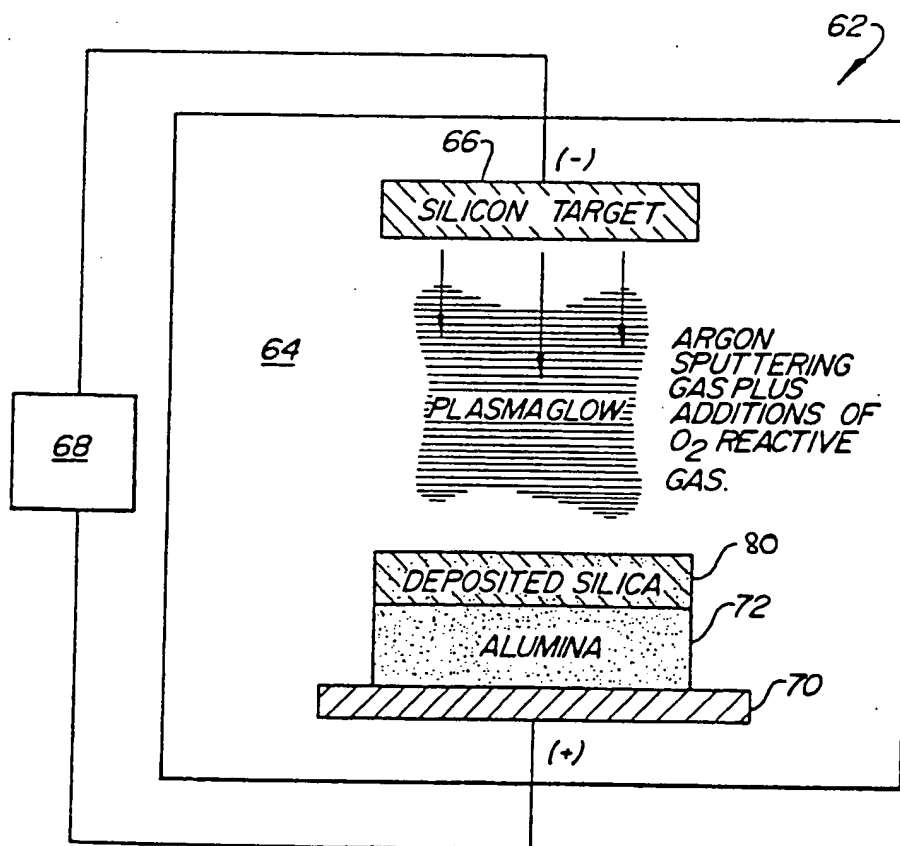


FIG-12

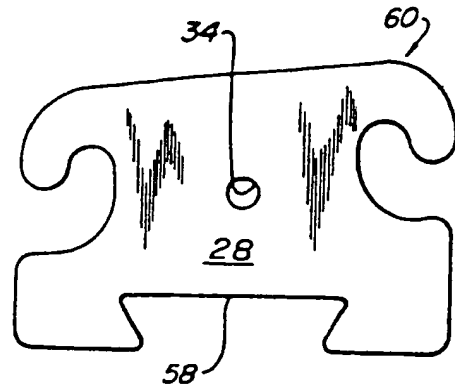


FIG-13

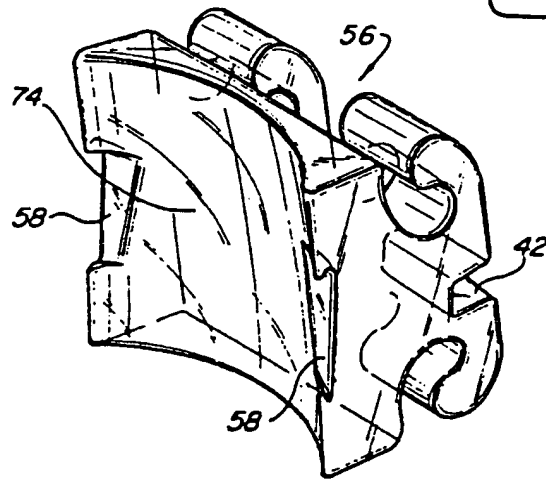


FIG-14

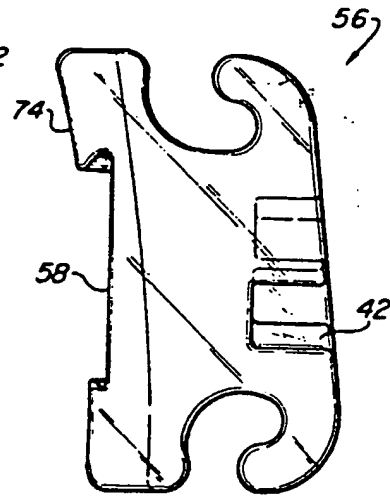


FIG-15

